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Abstract. For binary mixtures with fixed concentrations of the species, various relationships between the surface tensions and the concentrations are briefly reviewed.
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When we consider a binary mixture of two chemical species 1 and 2, in equilibrium with its vapor, one of the problems, experimentally as well as theoretically, is to predict how the corresponding surface tension depends on the composition of the mixture. Some relationship is expected which would give this surface tension, as an interpolation between the surface tensions of the two species when they are chemically pure. In this note, we briefly discuss various relation-ships based on thermodynamical considerations as well as other ones obtained more recently in the frame of Solid-On-Solid models of interfaces [1] and bulk statistical mechanical models of binary mixtures [2].

Thermodynamical semi-empirical equations

Let us use $\tau_{(1,2)|0}$ to denote the surface tension of a mixture of two species 1 and 2 and let $\tau_{1|0}$ and $\tau_{2|0}$ be the surface tensions of each species. In this section, we present several equations which have been derived, according to different assumptions, by using thermodynamical considerations.

For ideal or nearly ideal solutions, a fairly simple treatment, due to Guggenheim [3], leads to the following equation

$$e^{-\beta a\tau_{(1,2)|0}} = c_1 e^{-\beta a\tau_{1|0}} + c_2 e^{-\beta a\tau_{2|0}} \tag{1}$$

where c_1 is the fixed molar fraction of species 1 in the $(1,2)$ mixture, $c_2 = 1 - c_1$, the fixed molar fraction of species 2, a is the mean surface area per molecule, and $\beta = 1/kT$ is the inverse temperature.

A very simple relationship for the so called regular solutions comes from Prigogine and Defay [4], who proposed the equation

$$\tau_{(1,2)|0} = c_1\tau_{1|0} + c_2\tau_{2|0} - Kc_1c_2 \tag{2}$$

with K a semiempirical constant.

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A simple treatment due to Eberhart [5] assumes that the surface tension of a binary solution is linear in the surface composition, that is

$$\tau_{(1,2)|0} = c_1^s \tau_{1|0} + c_2^s \tau_{2|0} \tag{3}$$

where the c_i^s, $i = 1, 2$, denote the mole fraction near the surface of phase separation, and that the ratio c_1^s/c_1 is proportional to the ratio c_2^s/c_2.

Finally, when the surface tensions $\tau_{1|0}$ and $\tau_{2|0}$ differ appreciably, a semiempirical equation attributed to Szyszkowsky ([6], [7]) gives:

$$\frac{\tau_{(1,2)|0}}{\tau_{1|0}} = 1 - B \ln\left(1 + \frac{c_2}{A}\right) \tag{4}$$

where two characteristic constants A and B of the compounds have been used, and c_2 is the concentration of the species with the smaller surface tension.

We refer the reader to Adamson's book [8] (Chapter III, Section 4), and references therein, for a detailed discussion of the above equations.

Let us also mention that an extensive development for various types of non ideal solutions has been made by Defay, Prigogine and co–workers: see the monography [9].

Solid-On-Solid (SOS) models

Let us first consider the SOS model in dimension $d = 2$. We let $h_0, \dots, h_N \in \mathbb{R}$ be a collection of heights describing an interface. For simplicity, we assume that the energetic cost of the interface is proportional to its length, namely given by

$$H(J_\alpha; h_0 \cdots h_N) = J_\alpha \sum_{i=0}^{N-1} [1 + |h_{i+1} - h_i|] \tag{5}$$

where J_α represents the energetic cost per unit length for the interface. The associated density of free-energy or interfacial tension is then defined by

$$\tau(\beta J_\alpha) = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \ln Z(N, \beta J_\alpha) \tag{6}$$

where $Z(N, \beta J_\alpha)$ is the following partition function

$$Z(N, \beta J_\alpha) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta H(J_\alpha; h_0 \cdots h_N)} \delta(h_0 - 0)\delta(h_N - 0)$$

The quantities $\tau(\beta J_1)$ and $\tau(\beta J_2)$ will represent the surface tensions of two species 1, and 2.

To model the interface for binary mixtures, we will use the disordered generalization of the SOS model. Namely, we consider that the coupling per unit length is no more a constant but a random variable J. This variable may take two values J_1 and J_2 with probabilities c_1 and $c_2 = 1 - c_1$, where c_1 is physically the mole fraction of particles 1 in the bulk of the $(1, 2)$ mixture. This allows us to represent the interface by two sets of independent random variables $\{h_0, \dots, h_N\}$ and $\{J^0, \dots, J^{N-1}\}$. In this way, the interface can adjust its height h and, by moving or not molecules, also the corresponding energetic cost J taking into account the fixed concentration. In this approach the molecules of the mixture are not distinguishable and have similar size. Each site i is occupied by one molecule. The energetic cost of this interface is given by the Hamiltonian

$$H(J^0 \cdots J^{N-1}; h_0 \cdots h_N) = \sum_{i=0}^{N-1} J^i [1 + |h_{i+1} - h_i|] \tag{7}$$

where J^i may take the value J_1 or J_2 with probability c_1 or $c_2 = 1 - c_1$. The associated partition function is given by

$$Z_N(J^0 \cdots J^{N-1}) = \int_{-\infty}^{+\infty} dh_0 \cdots \int_{-\infty}^{+\infty} dh_N e^{-\beta H(J^0 \cdots J^{N-1}; h_0 \cdots h_N)} \delta(h_0)\delta(h_N)$$

It is well known that random systems are often related to disordered systems for which one has introduced the notion of quenched and annealed disorder. For the annealed case, the couplings are considered to be random and will be treated in the same way than the heights. For the quenched disorder, the couplings are frozen in a given configuration. There are then two ways to define the associated free energy density

$$\tau_{(1,2)|0}^{\text{quenched}} = -\frac{1}{\beta a} \lim_{N\to\infty} \frac{1}{N} \langle \ln Z_N(J^0 \cdots J^{N-1}) \rangle \tag{8}$$

and

$$\tau_{(1,2)|0}^{\text{annealed}} = -\frac{1}{\beta a} \lim_{N\to\infty} \frac{1}{N} \ln \langle Z_N(J^0 \cdots J^{N-1}) \rangle \tag{9}$$

where the average $\langle \cdot \rangle$ has to be taken with respect to the coupling distribution.

Using quenched disorder to compute the free energy, we obtain the following equation to express the surface tension of the mixture like a convex combination of the pure component surface tensions

$$\tau_{(1,2)|0}^{\text{quenched}} = c_1 \tau(\beta J_1) + c_2 \tau(\beta J_2)$$

This kind of formula is therefore valid when the system finds its equilibrium position within the configurations for a given set of couplings.

The other approach, i.e. if we use the annealed disorder, leads to :

$$e^{-\beta \tau_{(1,2)|0}^{\text{annealed}}} = c_1 e^{-\beta \tau(\beta J_1)} + c_2 e^{-\beta \tau(\beta J_2)}$$

Here, the variables J^i and h_i are treated on an equal basis. This implies that the molecules at the interface are sufficiently mobile to allow the interface to adjust itself, both in heights and in composition.

Bulk model of binary mixture

This Section is devoted to a discussion of the problem within a lattice bulk statistical mechanical model describing the binary mixture in equilibrium with its vapor. Studies of various models of binary lattice gases can be found in Refs. [10, 11].

Here, we consider a lattice gas system with two kinds of particles, where each lattice site can be in one of the three states, $0, 1, 2$, interpreted, respectively, as an empty site, a site occupied by a particle of the first kind of the model, and a site occupied by a particle of the second kind. Whenever the particles 2 are not allowed the system reduces to the usual Ising model, in its lattice gas version, with coupling constant $J_1/2$, and analogously, when particles 1 are not allowed, it reduces to the Ising model with coupling constant $J_2/2$. Namely, to each site $x \in \mathbb{Z}^d$, $d = 2, 3$, we associate a variable s_x taking values in the set $\Omega = \{0, 1, 2\}$. We will say that the site x is empty when $s_x = 0$ and that it is occupied otherwise. The energy of a configuration $\mathbf{s}_\Lambda = \{s_x\}_{x\in\Lambda}$ in a finite box $\Lambda \subset \mathbb{Z}^d$

is defined by

$$\begin{aligned} H_\Lambda(\mathbf{s}_\Lambda) &= \sum_{\langle x,y\rangle\subset\Lambda} E(s_x,s_y) \\ E(s_x,s_y) &= J_1\left[\delta(s_x,1)\delta(s_y,0)+\delta(s_x,0)\delta(s_y,1)\right] \\ &\quad +J_2\left[\delta(s_x,2)\delta(s_y,0)+\delta(s_x,0)\delta(s_y,2)\right] \end{aligned}$$

where $\langle x,y\rangle$ denote nearest neighbour pairs, δ is the usual Kronecker symbol $\delta(s,s')=1$ if $s=s'$ and $\delta(s,s')=0$ otherwise; J_1 and J_2 are positive constants. Notice that the bond energy satisfies:

$$\begin{aligned} &E(0,0)=E(1,1)=E(2,2)=E(1,2)=E(2,1)=0 \\ &E(0,1)=E(1,0)=J_1, E(0,2)=E(2,0)=J_2 \end{aligned}$$

Fixed densities of the three species are introduced through the canonical Gibbs ensemble of configurations $\mathbf{s}_\Lambda$ such that

$$\sum_{x\in\Lambda}\delta(s_x,0)=N_0,\ \sum_{x\in\Lambda}\delta(s_x,1)=N_1,\ \sum_{x\in\Lambda}\delta(s_x,2)=N_2$$

where the sum $N_0+N_1+N_2$ equals the number of sites of Λ. The associated partition functions with boundary condition bc are given by

$$Z_{bc}(\Lambda;N_1,N_2)=\sum_{\mathbf{s}_\Lambda\in\Omega^\Lambda} e^{-\beta H_\Lambda(\mathbf{s}_\Lambda)}\delta\left(\sum_{x\in\Lambda}\delta(s_x,1),N_1\right)\delta\left(\sum_{x\in\Lambda}\delta(s_x,2),N_2\right)\chi^{bc}(\mathbf{s}_\Lambda)$$

where $\chi^{bc}(\mathbf{s}_\Lambda)$ is a characteristic function standing for the boundary condition bc. We shall be interested in particular to the following boundary conditions:

- the empty boundary condition: $\chi^{\rm emp}(\mathbf{s}_\Lambda)=\prod_{x\in\partial\Lambda}\delta(s_x,0)$
- the mixture boundary condition: $\chi^{\rm mixt}(\mathbf{s}_\Lambda)=\prod_{x\in\partial\Lambda}(1-\delta(s_x,0))$
- the free boundary condition: $\chi^{\rm fr}(\mathbf{s}_\Lambda)=1$

where hereafter, the boundary $\partial\Lambda$ of the box Λ is the set of sites of Λ that have a nearest neighbour in $\Lambda^c=\mathbb{Z}^d\setminus\Lambda$.

The free energy per site corresponding to the above ensemble as a function of the densities ρ_1 and ρ_2 of the particles 1 and 2 is

$$f(\rho_1,\rho_2)=\lim_{\Lambda\uparrow\mathbb{Z}^d}-\frac{1}{\beta|\Lambda|}\ln Z_{bc}(\Lambda;[\rho_1|\Lambda|],[\rho_2|\Lambda|]) \tag{10}$$

where $[\,\cdot\,]$ denotes the integer part and the thermodynamic limit $\Lambda\uparrow\mathbb{Z}^d$ is taken in the van Hoove sense [12].

It is convenient to consider also a grand canonical Gibbs ensemble, which is conjugate to the previous ensemble, and whose partition function, in the box Λ is given by

$$\Xi_{bc}(\Lambda;\mu_1,\mu_2)=\sum_{\mathbf{s}_\Lambda\in\Omega^\Lambda} e^{-\beta H_\Lambda(\mathbf{s}_\Lambda)+\mu_1\sum_{x\in\Lambda}\delta(s_x,1)+\mu_2\sum_{x\in\Lambda}\delta(s_x,2)} \tag{11}$$

where the real numbers μ_1 and μ_2 replace as thermodynamic parameters the densities ρ_1 and ρ_2. The corresponding specific free energy, the pressure, is the limit

$$p(\mu_1,\mu_2)=\lim_{\Lambda\uparrow\mathbb{Z}^d}\frac{1}{|\Lambda|}\ln\Xi_{bc}(\Lambda;\mu_1,\mu_2) \tag{12}$$

Limits (10) and (12), which define the above free energies, exist. They are convex functions of their parameters and are related by the Legendre transformations

$$p(\mu_1,\mu_2) = \sup_{\rho_1,\rho_2}[\mu_1\rho_1+\mu_2\rho_2-\beta f(\rho_1,\rho_2)] \tag{13}$$

$$\beta f(\rho_1,\rho_2) = \sup_{\mu_1,\mu_2}[\mu_1\rho_1+\mu_2\rho_2-p(\mu_1,\mu_2)] \tag{14}$$

Finally we introduce the finite volume Gibbs measures (a specification) associated with the second ensemble:

$$\mathbb{P}^{bc}_\Lambda(\mathbf{s}_\Lambda) = \frac{e^{-\beta\tilde{H}_\Lambda(\mathbf{s}_\Lambda)}\chi^{bc}(\mathbf{s}_\Lambda)}{\Xi_{bc}(\Lambda;\mu_1,\mu_2)} \tag{15}$$

where $\tilde{H}_\Lambda(\mathbf{s}_\Lambda) = H_\Lambda(\mathbf{s}_\Lambda) - \frac{\mu_1}{\beta}\sum_{x\in\Lambda}\delta(s_x,1) - \frac{\mu_2}{\beta}\sum_{x\in\Lambda}\delta(s_x,2)$. They determine by the Dobrushin–Landford–Ruelle equations the set of Gibbs states $\mathcal{G}_\beta(\tilde{\mathcal{H}})$ on $\mathbb{Z}^d$ corresponding to the Hamiltonian $\tilde{H}$ at inverse temperature β (see e.g. [13]). A Gibbs state $\mathbb{P}\in\mathcal{G}_\beta(\tilde{\mathcal{H}})$ which equal the limit $\lim_{\Lambda\uparrow\mathbb{Z}^d}\mathbb{P}^{bc}_\Lambda(\cdot)$, is called Gibbs state with boundary condition *b.c.*

Ground states and low temperature analysis

In the zero temperature limit the Gibbs state with empty boundary condition is concentrated on the configuration with empty sites:

$$\lim_{\beta\to\infty}\mathbb{P}^{bc}_\Lambda(\mathrm{emp}_\Lambda) = 1 \tag{16}$$

where emp_Λ is the configuration where all the sites of Λ are empty, and this limit vanishes for any other configuration. Gibbs states at $\beta=\infty$ are called ground states.

Let, $R^{\mathrm{mixt}}_\Lambda(c) = \left\{s\in\Omega^\Lambda : \forall x\in\Lambda, s_x \not=0\right\}$, be the *restricted ensemble* of configurations in Λ with non empty sites, and $R^{\mathrm{mixt}}_\Lambda(c)$, $0\le c\le 1$ the subset of configurations of $R^{\mathrm{mixt}}_\Lambda$ with exactly $[c|\Lambda|]=N$ sites occupied by a particle of the specie 1 (and $|\Lambda|-[c|\Lambda|$ sites occupied by a particle of the specie 2).

With the mixture boundary conditions one gets by by Stirling's approximation and the principle of maximal term that

$$\lim_{\beta\to\infty}\mathbb{P}^{\mathrm{mixt}}_\Lambda(R^{\mathrm{mixt}}_\Lambda(c)) \underset{\Lambda\to\mathbb{Z}^d}{\longrightarrow} 1 \tag{17}$$

for $c=\frac{e^{\mu_1}}{e^{\mu_1}+e^{\mu_2}}$. This means that the ground state with mixt boundary conditions is concentrated on the restricted ensemble $R^{\mathrm{mixt}}(c)$ of configurations of non empty sites with concentration c of particles 1 and concentration $1-c$ of particles 2.

With free boundary conditions, one has for $c=\frac{e^{\mu_1}}{e^{\mu_1}+e^{\mu_2}}$

$$\lim_{\beta\to\infty}\mathbb{P}^{fr}_\Lambda(\mathrm{emp}_\Lambda) = 1/2,\ \lim_{\beta\to\infty}\mathbb{P}^{fr}_\Lambda(R^{\mathrm{mixt}}_\Lambda(c)) \underset{\Lambda\to\mathbb{Z}^d}{\longrightarrow} 1/2$$

Thus, with the above considerations, we get that for $e^{\mu_1}+e^{\mu_2}=1$, the configuration with empty sites coexists with the restricted ensemble $R^{\mathrm{mixt}}(c)$.

This analysis can be extend to the Gibbs states at low temperatures by using Pirogov-Sinai theory [14]. Actually, this theory allows to show that the low temperature phase diagram of the model is a small perturbation of the diagram of ground states the coexistence line given by the equation

$$\begin{aligned}\ln(e^{\mu_1^*}+e^{\mu_2^*}) = {} & e^{\mu_1^*-2d\beta J_1}+e^{\mu_2^*-2d\beta J_2} \\ & -\frac{(e^{\mu_1^*-\beta J_1}+e^{\mu_2^*-\beta J_2})^{2d}}{(e^{\mu_1^*}+e^{\mu_2^*})^{2d+1}} + O\left(e^{-(2d+1)\beta J}\right)\end{aligned}$$

where $J=\min\{J_1,J_2\}$.

In particular, introducing the infinite volume expectation $\langle\,\cdot\,\rangle^{\rm bc}(\mu_1,\mu_2)$ associated to the Gibbs measure (15), $\langle\,\cdot\,\rangle^{\rm bc}(\mu_1,\mu_2)=\lim_{\Lambda\uparrow\mathbb{Z}^d}\sum_{\mathbf{s}_\Lambda\in\Omega^\Lambda}\cdot\,\mathbb{P}^{\rm bc}_\Lambda(\mathbf{s}_\Lambda)$, we have for any $t\geq 0$:

$$\langle\delta(s_x,1)+\delta(s_x,2)\rangle^{\rm mixt}(\mu_1^*+t,\mu_2^*+t)\,\geq\,1-O\left(e^{-2d\beta J}\right)$$
$$\langle\delta(s_x,1)+\delta(s_x,2)\rangle^{\rm emp}(\mu_1^*-t,\mu_2^*-t)\,\leq\,O\left(e^{-2d\beta J}\right)$$

showing that the model exhibits at low temperature a first order phase transition at the coexistence line where the pressure is discontinuous.

Surface tensions

To introduce the surface tension between the mixture and the vapor, we consider the parallelepipedic box:

$$V=V_{L,M}=\Big\{(x_1,..,x_d)\in\mathbb{Z}^d:|x_i|\leq L,i=1,...,d-1;-M\leq x_d\leq M-1\Big\}$$

and let ∂_+V (respectively ∂_-V) be the set of sites of ∂V with $x_d\geq 0$ (respectively $x_d<0$). The boundary condition, $\chi^{\rm mixt,emp}(\mathbf{s}_V)=\prod_{x\in\partial_-V}(1-\delta(s_x,0))\prod_{x\in\partial_+V}\delta(s_x,0)$, enforces the existence of an interface between the mixture and the vapor and the interfacial tension between the mixture and the vapor is defined by the limit

$$\tau_{(1,2)|0}=-\frac{1}{\beta}\lim_{L\to\infty,M\to\infty}{\rm li}\,\frac{1}{(2L+1)^{d-1}}\ln\frac{\Xi_{\rm mixt,emp}(V;\mu_1^*,\mu_2^*)}{(\Xi_{\rm mixt}(V;\mu_1^*,\mu_2^*)\Xi_{\rm emp}(V;\mu_1^*,\mu_2^*))^{1/2}}$$

As mentioned previously, whenever either the particles 1 or the particles 2 are not allowed the system reduces to the usual Ising model in its lattice gas version. Thus, to define the surface tensions between each species of the mixture and the vapor, we introduce the configurations $n_V\in\{0,1\}^V$ of the lattice gas and the following partition functions

$$Q_\alpha(V)=\sum_{n_V\in\{0,1\}^V}e^{\beta J_\alpha\sum_{\langle x,y\rangle\subset V}[n_x(1-n_y)+(1-n_x)n_y]}\prod_{x\in\partial V}n_x$$
$$Q_{\alpha,0}(V)=\sum_{n_\Lambda\in\{0,1\}^V}e^{\beta J_\alpha\sum_{\langle x,y\rangle\subset V}[n_x(1-n_y)+(1-n_x)n_y]}\prod_{x\in\partial_-V}(1-n_x)\prod_{x\in\partial_+V}n_x$$

for $\alpha=1$ and $\alpha=2$. The interfacial tension between the species $\alpha=1,2$, and the vapor is the limit ([15, 16])

$$\tau_{\alpha,0}=\lim_{L\to\infty}\lim_{M\to\infty}\frac{F_\alpha(V)}{(2L+1)^{d-1}}$$

where $F_\alpha(V)=-\frac{1}{\beta}\ln\frac{Q_{\alpha,0}(V)}{Q_\alpha(V)}$. It is well known that the ratio $Q_{\alpha,0}(V)/Q_\alpha(V)$ can be expressed as a sum over interfaces which in this case are connected set of bonds or plaquettes of the dual lattice [17, 18]. Extracting the energy of the flat interface, the system can be written as a gas of excitations leading to $F_\alpha(V)=J_\alpha(2L+1)^{d-1}+F_\alpha^{\rm ex}(V)$. In two dimensions, $F_\alpha^{\rm ex}$ is the free energy of the gas of jumps of the Gallavotti's line [17]. In three dimensions, $F_\alpha^{\rm ex}$ is the free energy of the gas of walls of the Dobrushin's interface [18]. In both cases these free energies can be analyzed by cluster expansion techniques at low temperatures. Namely, the specific free energies $\mathcal{F}_\alpha=\lim_{L\to\infty}F_\alpha^{\rm ext}(V)/(2L+1)^{d-1}$ exist and are given by convergent expansions in term of the activities $e^{-\beta J_\alpha}$, giving

$$\tau_{\alpha,0}=J_\alpha+\mathcal{F}_\alpha \tag{18}$$

In addition

$$-\beta\mathcal{F}_\alpha = 2e^{-\beta J_\alpha} + O(e^{-2\beta J_\alpha}) \quad \text{for} \quad d=2 \tag{19}$$

$$-\beta\mathcal{F}_\alpha = 2e^{-4\beta J_\alpha} + O(e^{-6\beta J_\alpha}) \quad \text{for} \quad d=3 \tag{20}$$

Furthermore, in two dimensions the surface tension defined above is known to coincide with the one computed by Onsager [15]. We thus have an exact expression for $\tau_{\alpha,0}$, and for $\mathcal{F}_\alpha$, namely, $\beta\mathcal{F}_\alpha = \ln\tanh(\beta J_\alpha/2)$for βJ_α larger than the critical value $\ln(1+\sqrt{2})$.

Main result

The above surface tensions $\tau_{(1,2)|0}$, $\tau_{1,0}$ and $\tau_{2,0}$, are proved to satisfy, whenever β is large enough, the equation [2]:

$$e^{-\beta(\tau_{(1,2)|0}-\mathcal{F})} = c_1^* e^{-\beta(\tau_{1|0}-\mathcal{F}_1)} + c_2^* e^{-\beta(\tau_{2|0}-\mathcal{F}_2)} \tag{21}$$

The quantity $\mathcal{F}$ is the specific free energy (which can be expressed as a convergent series at low temperatures) of a gas of some geometrical objects called aggregates. In dimension $d=2$, those aggregates are the natural generalizations to our model of the jumps of Gallavotti's line and the leading term of the series giving this free energy $\mathcal{F}$ is

$$-\frac{2}{\beta}\frac{c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}}$$

In dimension $d=3$, they are the natural generalizations of the walls of the Dobrushin's interface and then the leading term of the series is

$$-\frac{1}{\beta}\frac{c_1^* e^{-5\beta J_1} + c_2^* e^{-5\beta J_2}}{c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2}} - \frac{1}{\beta}\frac{(c_1^* e^{-2\beta J_1} + c_2^* e^{-2\beta J_2})^4}{(c_1^* e^{-\beta J_1} + c_2^* e^{-\beta J_2})^4}$$

The coefficients c_1^* and c_2^* are related to the concentrations c_1 and c_2 of the particles 1 and the particles 2 through the equation

$$c_i^* = e^{\mu_i^* - p(\mu_1^*, \mu_2^*)}, i = 1, 2$$

This equation gives at low temperatures:

$$\begin{aligned} c_i^* = c_i \Big[1 - \left(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\right)^{2d} - 2d c_i e^{-\beta J_i} \left(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\right)^{2d-1} \\ -2(d+1)c_i \left(c_1 e^{-\beta J_1} + c_2 e^{-\beta J_2}\right)^{2d} + O\left(e^{-(2d+1)\beta \min\{J_1, J_2\}}\right) \Big] \end{aligned} \tag{22}$$

References

[1] J. De Coninck and J. Ruiz. Interfacial tensions for binary mixtures versus Solid–On–Solid models. *Preprint*, 2003.

[2] J. De Coninck, S. Miracle–Sole, and J. Ruiz. On the statistical mechanics and surface tensions of binary mixtures. *Preprint CPT–Marseille–2004/P.015, mparc 04–206, submitted to Journal of Statistical Physics.*

[3] E. A. Guggenheim. *Trans. Faraday Soc.*, **41**:150, 1945.

[4] R. Defay and I. Prigogine. *Trans. Faraday Soc.*, **46**:199, 1950.

[5] J. G. Eberhart. *J. Phys. Chem.*, **70**:1183, 1966.

[6] B. von Szyszkowsky. *J. Phys. Chem.*, **64**:385, 1908.

[7] H. P. Meissner and A. S. Michaels. *Ind. Eng. Chem.*, **42**:2782, 1949.

[8] A. W. Adamson. *Physical Chemistry of Surfaces.* John Wiley and Sons, New–York, 1997.

[9] R. Defay, I. Prigogine, A. Bellmans, and D. H Everett. *Surface tensions and absorption.* Longmans, Green and Co., London, 1966.

[10] J. C. Wheeler and B. Widom. *J. Chem. Phys.*, **52**:5334, 1970.

[11] J. L. Lebowitz and G. Gallavotti. Phases transitions in binary lattice gases. *J. Math. Phys.*, **12**:1129, 1971.
[12] D. Ruelle. *Statistical Mechanics: Rigorous Results*. Benjamin, New–York, Amsterdam, 1969.
[13] D. Ruelle. *Thermodynamic Formalism*. Addison Wesley, Reading, 1978.
[14] Ya. G. Sinai. *Theory of Phase Transitions: Rigorous Results*. Pergamon Press, London, 1982.
[15] A. Martin Lf, G. Gallavotti, and S. Miracle–Sole. Some problem connected with the coexistence of phase in the Ising model. In *Statistical mechanics and mathematical problems, Lecture Notes in Physics*, volume 20, page 162. Springer, Berlin, 1973.
[16] J. Bricmont, J. L. Lebowitz, and C.–E. Pfister. On the surface tensions of lattice systems. *Ann. N. Y. Acad. Sci.*, **337**:214, 1980.
[17] G. Gallavotti. Phase separation line in the two–dimensional Ising model. *Commun. Math. Phys.*, **27**:103, 1972.
[18] R. L. Dobrushin. Gibbs states describing the coexistence of phases for a three-dimensional Ising model. *Theory Prob. Appl.*, **17**:582, 1972.